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Discussions

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Interactive comment

Interactive comment on "Heteronuclear and Homonuclear Finite Pulse Radio Frequency Driven Recoupling" *by* Evgeny Nimerovsky et al.

Anonymous Referee #2

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The manuscript by Evgeny et.al proposes the use of RFDR for heteronuclear polarization transfer in the fast MAS regime. Instead of the routinely used time-independent effective Hamiltonians to describe recoupling conditions, the authors use the approach of time slicing typically employed in numerical simulation to follow the fate of different operators during heteronuclear fp-RFDR. They have explored several conditions for polarization transfer in presence and absence of CSA, offsets etc. Some experiments have been performed in the end to demonstrate the feasibility of heteronuclear polarization transfer. The experimental comparison demonstrates inferior performance than ramped-cp. I think using fp-RFDR for heteronuclear polarization transfer is an interesting idea and could potentially be beneficial in some special circumstances.

Having said the above I think there are several aspects that need to be carefully considered and explained before the potential of the method can be fuly appreciated.

The proposal of heteronuclear RFDR recoupling gets lost in the theoretical description and simulations under different conditions, model Hamiltonians, homo and heteronuclear cases. I think the section is too long and repeatedly the same message is conveyed through first 4-5 figures. From this description it is difficult to follow how the heteronuclear recoupling depends on factors such as the offset, duty factor etc as they seem very relevant in defining the recoupling condition/conditions. Both the role of offsets and duty factor is very crucial in defining the polarization transfer efficiency. I think the authors also realize this therefore the repeated one-D experimental data at different offset conditions. As is generally the norm, it would be useful to show the effective Hamiltonians (with relevant parameters) and then differentiate the conditions of homonuclear and heteronuclear polarization transfer. Lines 211-221: . . .. . . the first conclusion diverges – dependence on the ZQ Hamiltonian . . .. For AHT. I think the authors attempt to differentiate the homonuclear and heteronuclear polarization transfer conditions. This is not very clear and the authors should highlight it explicitly along with the aspects discussed above.

In principle one could follow the behaviour of the different operators in SIMPSON by setting the detection operator to the desired coherence. So I do not see the additional insights that one gains from the theoretical time slicing approach.

In Eq.4, I am wondering whether one can really get rid of the Dyson time ordering operator. I do not even see a clearly defined initial Hamiltonian. Before doing anything it is absolutely necessary to define internal interaction and rf Hamiltonian and systemically walk the reader through the analysis.

The idea of heteronuclear RFDR is not new and was proposed almost 25 years ago by Griffin and co-workers albeit at lower MAS frequency. (JMR A, 112, 191-198)

In my opinion, the presented experimental data is completely disconnected from the theoretical description and simulation provided in the beginning of the article.

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How does a 180 pulse applied with 47 kHz amplitude fit into 10 microsecond rotor period? Similarly, a 50 kHz 180-degree pulse on 1H with a 10-microsecond rotor period would imply a continuous pulsed rather than finite pulsed rfdr. are these errors necessary for experimental polarization transfer.

During heteronuclear RFDR, the homonuclear polarization transfer amongst proton and carbons is still operational. Its not clear how this simultaneous homonuclear polarization transfer impacts the heteronuclear polarization. There is also no discussion on this aspect. This is relevant in context of the conclusion drawn in line 480-481.

Eq 2.1, I think one 0.5 factor is extra.

The physical basis of model Hamiltonians is unclear. Also the condition where the particular model Hamiltonians will become relevant should be clearly highlighted.

Line 195-200: The authors compare buildup up of polarization due to IzSz Hamiltonian at slow and fast MAS. The conclusion that buildup rate is reversed is vague. I think the rate of polarization transfer critically dependence on the number of pulses applied. Since at 90 kHz MAS more pulses have been applied within 1-3 ms therefore the polarization builds up faster. I am bit surprised that the authors continuously discuss recoupling during the pulses in the manuscript but do not take this into account while discussing differential build up rates. In this light figure 2-4, needs a bit more careful analysis in terms of offsets and number of pules applied during the recoupling period.

The evolution of magnetization during finite pulse will lead to loss of magnetization so unlike other heteronuclear polarization transfer sequences such as CP where magnetization reach an equilibrium around 50%. Here one would expect the magnetization to rapidly decay. This is already visible in the appendix figures. However it would be good if one could show this both in experiments and simulation in a more realistic spin system. I think even in the ideal IS spin system the magnetization would decay after some finite number of pulses. It is very important to distinguish this aspect from regular heteronucler polarization methods.

Line 265-266: In case of the IS spin system, when the sum of the two offsets is equal to half the MAS frequency how can we understand the loss of magnetization. A similar phenomenon is not observed in case of homonuclear spin system. Its not clear why and what leads to the loss of polarization?

Figure 6: I am bit at a loss to understand what is it that differentiates figure 6a and 6b except the label IS and I2. For both the spin systems, offset is zero, csa's are zero and the same rf field is used i.e the rotating frame is the same. So why do differences occur. I am assuming the full Hamiltonian is used for the simulation since nothing is explicitly mentioned. Why do amplitudes of different operators change for the homonuclear case but not for the heteronuclear case.

In all heteronuclear simulations the same rf field is used on the two nuclei. Of course this is more challenging experimentally. It would be good to depict a plot of polarization transfer efficiency as a mismatch of the two rf amplitudes. This would also depict how forgiving the method is to rf missets and should be compared to a similar CP profile under identical conditions.

Figure 9: The transfer is $I1z \rightarrow I2z$ i.e homonuclear but heteronuclear spin system parameters are used. Is this correct or it does not matter, not clear?

It is claimed that polarization transfer to aromatic group during hetRFDR is comparable to CP. However it is not clear whether rCP was optimized for broadband polarization transfer or is it compared directly to aromatic peak optimized rCP. It would also help to have experimental polarization buildup curves as a function of mixing time for both transfer.

The low S/N noise due to 13C/15N detection obscures a meaningful comparison between hetRFDR and CP transfer. It might be meaningful to use two hetRFDR to do proton detection and clearly have the sensitivity to highlight the gain on different chemical moieties.

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Minor comments a) line 183 . . . .pink lines . . . . pink and magenta are interchangeably used in figure caption b) several figure captions eq 2.2c is referred as scalar Hamiltonian. c) Several instances of use of . . . .. "Microscopic and macroscopic" magnetization –→ I think the author try to imply single crystal and powder averaging. Its better to use the later to be consistent with literature unless something more is implied. d) Several instances: velocity of magnetization transfer is used -→ one should consider using polarization transfer or buildup rates. e) Line 438: reference spell check.

I feel there are number of issues with the manuscript. Theory, simulations and experiments do not seem to provide a meaningful perspective for the proposed heteronuclear RFDR recoupling. Authors should really reconsider streamlining the theory and experiments to make the manuscript appealing.

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